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(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
16 January 2003 (16.01.2003)

PCT

(10) International Publication Number  
WO 03/004547 A2

- (51) International Patent Classification<sup>7</sup>: C08G 63/82
- (21) International Application Number: PCT/US02/18991
- (22) International Filing Date: 17 June 2002 (17.06.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/302,848 2 July 2001 (02.07.2001) US
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- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

- without international search report and to be republished upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: PROCEDURE FOR THE MANUFACTURE OF POLYALKENE TEREPHTHALATES

(57) Abstract: Procedure for the manufacture of polyalkene terephthalate The invention concerns a procedure for the manufacture of polyalkene terephthalate, in which both the transesterification and the polycondensation steps are performed with one and the same catalyst. According to the invention, hydrotalcites and hydrotalcite-like compounds of general formula  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-}x/n?)_m \cdot m H_2O$  are used alone or in combination with suitable stabilizers, for instance phosphorus compounds or derivatives of ortho-tert.-butyl-phenol, without requiring deactivation of the transesterification catalyst. The M(II) in the general formula stands for divalent metals, in particular for magnesium, zinc, nickel, copper, iron(II) or cobalt(II). M(III) are trivalent metals, for instance aluminum or iron(III). A are anions, such as carbonates, borates or titanil compounds.

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## PROCEDURE FOR THE MANUFACTURE OF POLYALKENE TEREPHTHALATES

The invention concerns a procedure for the manufacture of polyalkene terephthalates, in which both the transesterification and the polycondensation steps are performed with the same catalyst.

At the present time there exist two commercial procedures for the manufacture of polyalkene terephthalate, in particular of polyethylene terephthalate. The variant used in particular in the manufacture of polyethylene terephthalate for food packaging (bottles) is based on the esterification of pure terephthalic acid. The older procedure, based on dimethyl terephthalate, is still used today on a large scale in the manufacture of polyester fibers. In this procedure it is necessary to accelerate both the transesterification of dimethyl terephthalate with ethylene glycol to bis-(2-hydroxy-ethyl)-terephthalate oligomers and also the subsequent polycondensation of the oligomers using suitable catalysts (WO 9213022; EP 0447110, JP 63 278 927; DE 2,014,818; JP 46 028 788; DE 1,917,124; FR 1,418,536).

The reaction of dimethyl terephthalate with ethylene glycol is preferably catalyzed by acetates of transition metals. Patents WO 9213022, JP 63 278 927, DE 1,917,124 and EP 0447110 describe manganese compounds as catalysts for transesterification. Zinc salts (DE 2,014,818; FR 1,481,536) and calcium salts (JP 46 028 788) can also be used as catalysts in this procedural step. Following transesterification, the catalytically active compounds are deactivated, since they accelerate the thermal degradation of the polyester under the conditions of polycondensation and of processing.

Patent WO 9213022 describes the use of germanium compounds in the polycondensation step, while patents EP 0447110, DE 2,014,818, DE 1,917,124 and FR 1,481,536 use antimony compounds as polycondensation catalysts. The object of Japanese patents JP 63 278 927 and JP 46 028 818 is the use of titanium compounds as catalyst for polycondensation.

Japanese patent JP 04304231 describes the use of titanium compounds for transesterification and of germanium oxide in the polycondensation step. Titanium compounds as polycondensation catalysts are also protected (US 4115371; JP 06100679).

It is also known that hydrotalcites and hydrotalcite-like substances can be used as heterogeneously acting catalysts in polycondensation (WO 01 42335). US patent 5,017,680 describes the use of a catalyst mixture of manganese and/or calcium, cobalt or zinc compounds in the transesterification step. The antimony compound necessary for poly-

condensation is added together with the transesterification catalysts during the first procedural step. The transesterification catalysts are deactivated also in this patent, with a suitable phosphorus compound, prior to polycondensation.

US patent 3,457,239 describes the use of lead(II) fluoride as catalytically active component in both procedural steps.

The use of heavy metal-containing transesterification catalysts (manganese, lead, zinc) leads to restricted use possibilities for these polyesters.

The invention is based on the task of finding a heavy metal-free catalyst system that is capable of catalyzing both the transesterification and the polycondensation step in the manufacture of polyesters, in particular of polyalkene terephthalates, without having to accept limitations regarding selectivity and reaction rate.

It was surprisingly found that hydrotalcites and hydrotalcite-like compounds of general formula  $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}(A^{n-})_x \cdot m H_2O$  are able to catalyze, alone or in combination with suitable stabilizers such as phosphorus compounds or derivatives of ortho-tert.-butyl-phenol, the transesterification and the polycondensation step in the manufacture of polyesters, in particular of polyalkene terephthalates, without requiring a deactivation of the transesterification catalyst. The M(II) in the general formula stands for a divalent metal, in particular for magnesium, zinc, nickel, copper, iron(II) or cobalt(II). M(III) are trivalent metals, such as aluminum or iron(III). A represents anions, such as carbonates, borates or titanate compounds.

The particle size of the hydrotalcites and hydrotalcite-like compounds used lies in the range of 0.1-20  $\mu m$ , preferably in the range of 0.5-10  $\mu m$ .

The calcination of the hydrotalcites and hydrotalcite-like compounds used occurs at temperatures between 250 and 900°C, preferably between 450 and 850°C.

The phosphorus compounds used can be phosphoric acid esters or esters of phosphorous acid that have at least one hydrolyzable P-O bond and preferably, at least one o-tert.-butyl-phenol group.

Suitable stabilizers are also purely organic compounds that have at least one o-tert.-butyl-phenol group.

The catalyst system according to the invention is composed of the hydrotalcite or the hydrotalcite-like compound and the stabilizer, in a ratio of 1:0.5 to 1:4, preferably of 1:1 to 1:2.

In combination with the stabilizers, the untreated and the calcined hydrotalcite-like compounds show increased catalytic activity, compared to traditional catalysts, for transesterification and for polycondensation. These catalyst/stabilizer systems are physiologically harmless and thereby differ from the conventionally used heavy metal systems.

It was found that these substances, independently of their elemental composition, have a high catalytic activity in both procedural steps (transesterification and polycondensation). With these catalyst systems, transesterification is performed under normal or overpressure, at temperatures between 180°C and 260°C and an excess of ethylene glycol, relative to dimethyl-terephthalate and/or the esters of other aromatic dicarboxylic acids. With these catalyst system the polycondensation occurs at reduced pressure and at temperatures of 230°C to 280°C, in the liquid phase.

The addition of the catalysts can be accomplished either by adding the total amount of catalyst prior to the transesterification, or by dividing the addition, with at least 50 % added before the transesterification and the rest before the polycondensation step.

The addition of stabilizers leads to an increased thermal stability of the polyesters under the conditions of polycondensation and the subsequent processing. The generation of highly volatile impurities, such as acetaldehyde as product of the thermal decomposition of polyesters based on ethylene glycol, and the discoloration can thereby be substantially repressed.

The invention will be clarified below by means of implementation examples.

The intrinsic viscosity (IV) of the polyesters synthesized was determined on an instrument of the Schott company (AVSPro), on 250 mg resin dissolved in 50 ml phenol/dichlorobenzene (1:1).

#### 1. Realization of the transesterification

The manufacture of the precondensate by transesterification of dimethyl-terephthalate with ethylene glycol to bis-(2-hydroxyethyl)-terephthalate oligomers was performed in a 2 L four-necked flask with distillation head, thermometer, stirrer and gas inlet tube. In each case, preplace 2 mol dimethyl-terephthalate, 8 mol ethylene glycol, the catalyst and the stabilizer. Heat with stirring to 150°C. At this temperature the methanol released begins to distill off, in most cases. The transesterification product is then heated to up to 230°C, under constant stirring and distillation of methanol. In order to remove the methanol and part of the ethylene

glycol excess as completely as possible from the reaction mixture, wash with nitrogen for approximately 15 min, at this temperature. The cooled but still liquid reaction product is next transferred to a steel dish, where it slowly crystallizes out upon cooling. Once the product has cooled, it is ground and subsequently used in the polycondensation step.

## 2. Realization of the polycondensation

In a 250 ml single neck flask with stirrer and distillation head, preplace 100 g catalyst and stabilizer-containing precondensate, consisting of terephthalic acid-ethylene glycol oligomers, with a mean molecular weight of 800 g/mol, together with fresh catalyst in one part of the experiments. Evacuate the equipment to approx. 0.5 mbar and aerate with nitrogen. This process was repeated a total of 3 times. Immerse the glass flask in a salt bath at 280°C and allow the precondensate to melt at this temperature. As soon as melting is complete, carefully apply a vacuum.

Under constant stirring and distilling off the released ethylene glycol, perform the polycondensation at a temperature of 280°C.

After stopping the polycondensation by aeration with nitrogen, allow the product to cool in the flask and characterize the polyester after separating it from the adhering glass.

Table 1 summarizes the results for the experiments performed.

Table 1 Realization of the transesterification and polycondensation in the presence of hydrotalcite and hydrotalcite-like compounds

| Experm. No.              | Transesterification              |                       |   |                       |             | Polycondensation    |                          |                            |                     |
|--------------------------|----------------------------------|-----------------------|---|-----------------------|-------------|---------------------|--------------------------|----------------------------|---------------------|
|                          | Catalyst                         | Concentrat ion (ppm)  | Stabilizer                              | Concentra- tion (ppm) | Yield (%) * | Reaction time (min) | Catalyst added           | Intrinsic viscosity (dl/g) | Reaction time (min) |
| 1<br>(Comparison expl.)  | MgAc2<br>MnAc2<br>ZnAc2<br>CoAc2 | 120<br>30<br>50<br>90 | Phospho-ric acid (add after transester. | 220                   | 92.5        | 300                 | SbAc3 (540 ppm)          | 0.707                      | 120                 |
| 2<br>(per the invention) | Pural Mg 61 HT *1)               | 150                   |   |                       | 90.1        | 200                 |                          | 0.6746                     | 120                 |
| 3 (per the invention)    | Pural Mg 61 HT                   | 150                   |   |                       | 90.1        | 200                 | Pural Mg 61 HT (150 ppm) | 0.7634                     | 120                 |
| 4 (per the invention)    | Pural Mg 61 HT                   | 250                   |   |                       | 93.5        | 200                 |                          | 0.619                      | 120                 |
| 5 (per the invention)    | Pural Mg 61 HT                   | 250                   | Irganox 1010 *2)                        | 250                   | 95.05       | 290                 |                          | 0.702                      | 120                 |
| Experm. No.              | Transesterification              |                       |   |                       |             | Polycondensation    |                          |                            |                     |
|                          | Catalyst                         | Concentrat ion (ppm)  | Stabilizer                              | Concentra- tion (ppm) | Yield (%) * | Reaction time (min) | Catalyst added           | Intrinsic viscosity (dl/g) | Reaction time (min) |
| 6 (per the invention)    | Pural Mg 61 HT                   | 250                   | Irganox PEP-Q *2)                       | 250                   | 93.8        | 275                 |                          | 0.7135                     | 120                 |
| 7 (per the invention)    | Pural Mg 61 HT                   | 250                   | Irganox 1222 *2)                        | 250                   | 96.3        | 255                 |                          | 0.6791                     | 120                 |
| 8 (per the invention)    | Pural Mg 61 HT<br>calc. 450°     | 250                   | Irganox 1010                            | 250                   | 97.5        | 330                 |                          | 0.7585                     | 120                 |

|                        |                              |                     |              |                     |             |                     |                       |                            |                     |
|------------------------|------------------------------|---------------------|--------------|---------------------|-------------|---------------------|-----------------------|----------------------------|---------------------|
| 9 (per the invention)  | Pural Mg 61 HT<br>calc. 650° | 250                 | Irganox 1010 | 250                 | 96.9        | 330                 | 0.7048                | 120                        |                     |
| 10 (per the invention) | Pural Mg 61 HT<br>calc. 850° | 250                 | Irganox 1010 | 250                 | 98.1        | 275                 | 0.7460                | 120                        |                     |
| 11 (per the invention) | Zn/Al HT<br>*3)              | 125                 | Irganox 1010 | 250                 | 98.1        | 150                 | Zn/Al HT<br>(125 ppm) | 120                        |                     |
| Experim. No.           | Transesterification          |                     |              | Polycondensation    |             |                     |                       |                            |                     |
|                        | Catalyst                     | Concentration (ppm) | Stabilizer   | Concentration (ppm) | Yield (%) * | Reaction time (min) | Catalyst added        | Intrinsic viscosity (dl/g) | Reaction time (min) |
| 13 (per the invention) | Zn/Al HT<br>*3)              | 125                 | Irganox 1010 | 250                 | 98.1        | 150                 | Zn/Al HT<br>(500 ppm) | 0.6612                     | 120                 |

\* The yield of the transesterification reaction is relative to ml of distilled methanol.

\*1) Hydrotalcite based on magnesium/aluminum compounds of the SASOL company

\*2) Irganox 1010, Irganox 1222 and Irganox PEP-Q: stabilizers based on phosphorus compounds of the CIBA-GEIGY company

\*3) Hydrotalcite-like compound  $Zn_6Al_2(OH)_4CO_3 \cdot 4H_2O$ ; based on Al and Zn nitrate



Table 1 makes clear the catalytic effect of the hydrotalcites and hydrotalcite-like compounds both in the transesterification and also the polycondensation step. The activity of the catalysts listed is at least comparable to the traditionally used catalyst systems, in the two reactions.

5       The stabilizers are added in view of the processing of the polyesters. The discoloration and formation of highly volatile degradation products can be substantially curtailed by the addition of these substances, without losing in selectivity and activity of the catalysts in the process.

10       The polyesters synthesized in this manner can be used both as starting material for fibers and also as material for food packaging (bottles, sheets, etc.).

It is obvious that besides the variants listed as implementation examples, other combinations of catalysts according to the invention and known catalysts are conceivable.

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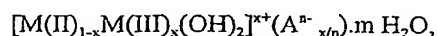
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## PATENT CLAIMS

1. Procedure for the manufacture of polyalkene terephthalate, characterized by both the  
 5 transesterification and the polycondensation steps being catalyzed by hydrotalcites or  
 hydrotalcite-like compounds of general formula



alone or in combination with stabilizers, where M(II) stands for divalent metals, M(III)  
 for trivalent metals and A for anions, without requiring deactivation of the  
 10 transesterification catalyst.

2. Procedure for the manufacture of polyalkene terephthalate according to claim 1,  
 characterized by M(II) being magnesium, zinc, nickel, copper, iron(II) or cobalt(II);  
 M(III) is aluminum or iron(III) and A are carbonates, borates or titanyle compounds.

3. Procedure for the manufacture of polyalkene terephthalate according to claims 1 and 2,  
 characterized by the stabilizers used being phosphorus compounds or derivatives of  
 ortho-tert.-butyl-phenol.

4. Procedure for the manufacture of polyalkene terephthalate according to claim 3,  
 characterized by the phosphorus compounds used being phosphoric acid esters or  
 phosphorous acid esters, that have at least one hydrolyzable P-O bond and preferably at  
 least one ortho-tert.-butyl-phenol group.

5. Procedure for the manufacture of polyalkene terephthalate according to claims 1 through  
 4, characterized by the catalyst system used having a ratio of hydrotalcite or  
 hydrotalcite-like compound to stabilizer in the range of 1:0.5 to 1:6, preferably of 1:1 to  
 1:2.

6. Procedure for the manufacture of polyalkene terephthalate according to claims 1 through  
 5, characterized by the amount of catalyst added being of 100 to 50 % before  
 transesterification and of 0 to 50% before the polycondensation step.

7. Procedure for the manufacture of polyalkene terephthalate according to claims 1 through 6, characterized by the particle size of the hydrotalcites or hydrotalcite-like compounds used being in the range of 0.1 to 20  $\mu\text{m}$ , preferably in the range of 1 to 10  $\mu\text{m}$ .
- 5 8. Procedure for the manufacture of polyalkene terephthalate according to claims 1 through 7, characterized by the calcination of the hydrotalcites or hydrotalcite-like compounds used occurring at temperatures between 100 and 900  $^{\circ}\text{C}$ , preferably between 450 and 850  $^{\circ}\text{C}$ .
- 10 9. Procedure for the manufacture of polyalkene terephthalate according to claims 1 through 8, characterized by the transesterification being performed under normal or increased pressure, at temperatures between 180 $^{\circ}\text{C}$  and 260 $^{\circ}\text{C}$  and the polycondensation under reduced pressure at temperatures of 230 $^{\circ}\text{C}$  to 280 $^{\circ}\text{C}$  in the liquid phase.
- 15 10. Utilization of polyalkene terephthalate, produced according to claims 1-9, for the manufacture of fibers as well as packaging, such as bottles and sheets.